

**NOVEL HIGH-STRENGTH, MAGNETIC,**  
**NANOSTRUCTURED ALLOYS**

by

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## **NOVEL HIGH-STRENGTH, MAGNETIC, NANOSTRUCTURED ALLOYS**

### **Government Interests**

5           The United States Government has rights in this invention under Contract Nos. NIST-60NANB2DD12D and NSF-DMR0314209 between the United States National Science Foundation (NSF), the United States National Institute of Standards and Technology (NIST) and Dartmouth College.

### **Field of the Invention**

10           The invention generally relates to novel alloys and methods of producing alloys. More specifically, the alloys are high-strength, nanostructured alloys that possess magnetic properties.

### **Background of the Invention**

15           Basic research in the field of alloy materials seeks to find improved materials, such as those that are lighter, stronger, or less expensive to make. In other contexts, improved materials may have increased resistance to weather, chemicals, or friction, in an intended environment of use. Equipment that incorporates these new materials in component parts  
20           may have a longer service life or require less maintenance. Improved performance advantageously requires fewer maintenance operations, provides longer service life of component parts, or achieves an improved performance level of components that are made of these new materials. From a cost of manufacture standpoint, it is desirable for these new materials to be made from readily available and highly affordable natural resources.

25           Researchers and engineers tasked with the design of these new materials have begun to conceive of not only better materials with improved properties, but materials with a multitude of desirable properties. These so-called multi-functional materials have a combination of useful physical, optical, magnetic, conductive or other properties.

30           Spinodal decomposition is one technique that may be used to enhance the strength of an alloy. Spinodal decomposition processes for use in alloy processing are described, for example, in Ramanarayan and Abinandan, *Spinodal decomposition in fine grained materials*, Bltn. Matter. Sci. Vol. 26, No. 1, 189-192(January 2003). Transition phase kinetics of

spinodal decomposition systems may be explored using X-ray scattering as described in Mainville et al., *X-ray scattering Study of Early Stage Spinodal Decomposition in Al<sub>0.62</sub>Zn<sub>0.38</sub>*, Phys. Review Lett. Vol. 78, No. 14, 2787-2790 (1977). The Toughmet™ Cu-Ni-Sn alloys that are commercially available from Brush Wellman of Lorain, Ohio are one example of spinodal alloys used for structural applications.

There is a continuing need for superior alloys, especially magnetic alloys having improved strength, structural and magnetic characteristics.

### **Summary of the Invention**

Alloys of the present disclosure address the problems outlined above and advance the art by providing alloys with exceptional strength or hardness over a wide temperature range. In addition, the materials may demonstrate good magnetic characteristics. The alloys may be incorporated into machine and industrial parts. The alloys may be used to make large, high-strength parts that cannot be made by extrusion, forging or cold working techniques. Additionally, the alloys may be suitable for applications requiring high-strength, wear resistant parts including but not limited to: engines, bearings, bushings, stators, washers, seals, rotors, fasteners, stamping plates, dies, valves, punches, automobile parts, aircraft parts, and drilling and mining parts.

Materials described herein may demonstrate high impact strength, fatigue resistance, and toughness under harsh conditions. They may also have superior wear and corrosion resistance.

Alloy constituents may include a substantial amount of one or more magnetic elements selected from transitional metals and rare earth metals. In particular, the alloy contains iron, nickel, manganese, and aluminum to which may be added vanadium, chromium, cobalt, molybdenum, and ruthenium. This concept is represented by a macroscopic formula including the overall alloy:

Formula (1) 
$$\text{Fe}_a\text{Ni}_b\text{Mn}_c\text{Al}_d\text{M}_e,$$

wherein M may be vanadium, chromium, cobalt, molybdenum, ruthenium or combinations thereof,

a ranges from 16 to 70;

b ranges from 19 to 35;

c ranges from 18 to 33;

d ranges from 18 to 33; and  
e ranges from 0 to 5.

Another aspect of the alloy may be a heat treatment process that results in spinodal  
5 decomposition leaving at least two intermetallic phases of different structure and  
stoichiometry. Thus, the macroscopic formula above pertains to the overall composition, but  
the macroscopic composition has nanostructure or microstructure of localized phase variances  
in composition and ordering. Generally, growth processes that result in lattice phase  
separations may derive from two mechanisms—nucleation or spinodal. In nucleation, nuclei  
10 form and lattice growth occurs on the individual nuclei. An energy barrier must be met to  
drive the growth. The lattice phases are well defined, such that a lattice structure arises from  
a matrix which may be amorphous. Another mechanism, that of spinodal decomposition, is a  
spontaneous clustering reaction that may occur in a homogeneous supersaturated solution,  
which may be a solid or liquid solution. The solution is unstable against infinitesimal  
15 fluctuations in density or composition, and so thermodynamics favor separation into two  
phases of differing composition and interconnected morphology. Lattice phase boundaries  
are diffuse and gradually become sharp. Spinodal decomposition of an alloy is possible when  
different metal atoms are of similar size; thus avoiding large scale diffusion which results in  
precipitation. The presence of two phases gives rise to large composition variations which  
20 cause coherency strains that strengthen the alloy.

In one aspect, the alloy is formed using reagents, compositions, and methods that are  
useful for the production of the disclosed alloys. Certain techniques and methods are useful  
for analysis of the properties and chemical formulations of the novel alloys' disclosed herein.

These and various other features as well as advantages which characterize the present  
25 invention will be apparent from a reading of the following detailed description and a review  
of the associated drawings.

### **Brief Description of the Drawings**

FIG. 1 is a phase diagram schematically illustrating one spinodal decomposition  
30 process;

FIG. 2 is a transition electron micrograph of an exemplary intermetallic compound;

FIG. 3 is a plot showing yield stress versus temperature for  $\text{Fe}_{30}\text{Ni}_{20}\text{Mn}_{25}\text{Al}_{25}$ ;

FIG. 4 is a magnetic hysteresis plot for the two phase alloy,  $\text{Fe}_{30}\text{Ni}_{20}\text{Mn}_{25}\text{Al}_{25}$ ;  
FIG. 5 is a magnetic hysteresis plot for the b.c.c phase,  $\text{Fe}_{49}\text{Ni}_{12}\text{Mn}_{30}\text{Al}_{19}$ ; and  
FIG. 6 is a magnetic hysteresis plot for the B2 phase,  $\text{Fe}_{13}\text{Ni}_{34}\text{Mn}_{14}\text{Al}_{39}$ .

### **Detailed Description**

The following definitions are provided to facilitate understanding of certain terms used frequently herein and are not meant to limit the scope of the present disclosure:

The terms “alloy”, “intermetallic compound”, and “intermetallic compositions” are interchangeable. They refer to compounds containing at least two elements selected from metals and/or metalloids.

“Ordered” refers to a uniform arrangement of atoms within a chemical structure. Alternatively, the term “ordered” may mean a uniform arrangement of electrons within a magnetic structure.

As is known in the art, spinodal decomposition is a continuous diffusion process in which there is no nucleation step. A plurality of chemically different phases result from a migration of atoms, without the formation of precipitates. Fig. 1 is a phase diagram showing one spinodal decomposition process that varies as a function of temperature  $T$  and intermetallic composition  $X_B$ . A homogenous composition or phase  $\alpha$  exists at temperatures above  $T_m$ . An immiscibility dome contains a spinodal decomposition region that is flanked by nucleation zones 106, 108. At temperatures below  $T_m$ , phases  $\alpha_1$  and  $\alpha_2$  exist, each associated with an adjacent nucleation zone 106, 108, and these regions of Fig. 1 below  $T_m$  are sometimes referred to as the “miscibility gap.” The spinodal decomposition region 104 may be regarded as a stable or metastable region that contains both phases  $\alpha_1$  and  $\alpha_2$ , and where atom migration is enabled by a miscibility difference between the phases  $\alpha_1$  and  $\alpha_2$ . The structure of each phase  $\alpha_1$ ,  $\alpha_2$  within spinodal decomposition region 104 is usually continuous throughout the grains and continues up to the grain boundaries. The presence of two phases  $\alpha_1$ ,  $\alpha_2$ , with corresponding composition variations, increases coherency strain thereby strengthening the material.

The alloys disclosed herein may be used under extreme conditions, for example, elevated temperatures and pressures or highly resistive conditions. Furthermore, the alloys disclosed herein can be used in any known application currently utilizing a high-strength alloy.

Having generally described the invention, the same will be more readily understood by reference to the following examples, which are provided by way of illustration and are not intended as limiting.

### EXAMPLES

5           The following examples set forth preferred materials and methods for use in making the disclosed alloys. The examples teach by way of illustration, not by limitation, and so should not be interpreted as unduly narrow.

#### Example 1

##### Preparation and Characterization of $\text{Fe}_{30}\text{Ni}_{20}\text{Mn}_{25}\text{Al}_{25}$

10           A quaternary alloy of  $\text{Fe}_{30}\text{Ni}_{20}\text{Mn}_{25}\text{Al}_{25}$  composition was prepared by well known arc melting and casting techniques. A quantity of material including 24g Fe, 17g Ni, 22g Mn, and 10g Al was placed in a water-cooled copper mold and heated until molten using the arc melting technique. Ingots were flipped and melted a minimum of three times to ensure mixing. Quenching was done by allowing the alloy to rapidly cool in the copper mold to a  
15           temperature of  $\sim 30^{\circ}\text{C}$  in approximately 10 minutes. Fig. 2 is a TEM image taken along the {100} axis. The alloy had nanostructure including 50 - 60 nm wide B2-structured plates that were spaced 40-50 nm apart. The plates were separated by a matrix material. The plates lie along axis {100} and have faces 200 that are consistent with a body centered cubic (b.c.c.) matrix. The nanostructure appears to have developed through spinodal decomposition in  
20           which either the B2 structure formed at high temperatures and the b.c.c. second phase formed spinodally upon cooling, or the b.c.c. structure formed at high temperatures and the B2 phase formed spinodally at lower temperatures. Due to the significant composition differences between the phases there is a large coherency strain, which gives rise to a very strong alloy.

          The alloy was characterized using analytical techniques that are well known in the art.  
25           Chemical composition was determined by energy dispersive spectroscopy (EDS). Table 1 reports the composition data for the respective b.c.c. and B2 phases. Magnetic studies were performed on 5-25 mg samples using a LakeShore Model 668 VSM capable of measuring magnetic fields up to 1.4T. Structural data was obtained using a Siemens D5000  
          Diffractionmeter with a Kevex PSI silicon detector in the range of  $10\text{-}130^{\circ} 2\theta$ , using an  
30           instrument that was calibrated against an alumina standard purchased from the National Institute of Standards (NIST). Yield strength was determined using a MTS 810 mechanical

testing system. Transmission electron microscopy (TEM) was performed on either a JEOL 2000FX or a Philips CM 200, see Fig. 2.

Individual samples of each phase were prepared by the above mentioned arc melting and casting techniques. The b.c.c. phase and B2 phase alloys were formed by placing 34.5g Fe, 1.48g Ni, 21.8g Mn and 6.45g of Al and 8.37g Fe, 23.0g Ni, 9.3g Mn and 12.7g Al, respectively, in a water cooled copper mold and heating until molten using the arc melting technique. Samples were flipped and melted three times to ensure mixing. Quenching consisted of allowing the molten ingot to rapidly cool in the copper mold to  $\sim 30^{\circ}\text{C}$  in  $\sim 10$  minutes. The magnetic properties of the individual phases were measured three times with average coercivities and saturation magnetizations of 63 G and 0.03 T for the B2 phase and 27 G and 0.48 T for the b.c.c. phase, respectively.  $\text{Fe}_{30}\text{Ni}_{20}\text{Mn}_{25}\text{Al}_{25}$  displayed a coercivity and saturation magnetization of 72 G and 0.31T, respectively, at 298 K. Hysteresis plots of two phase alloys including the b.c.c constituent and the B2 constituent are shown in Figs 4-6, respectively, where Fig. 4 is the plot for the alloy, Fig. 5 is that for the b.c.c. phase and Fig. 6 that for the B2 phase. With regard to Fig. 6, it is noted that the plot could have been shifted to pass through the 0,0 locus by calibrating the magnetometer to account for any moment offset.

Room temperature hardness of the two phase alloy as well as the b.c.c. and B2 constituent phases was determined by taking the average of five measurements from a Leitz Microhardness indenter with a 200g load. Results are given in Table 2.

The yield strength at 298 K was determined to be 1300 MPa and 1490 MPa at 653 K. The latter strength for the present alloy is higher than the best current nickel-based superalloys, such as IN718 (1360 MPa), which contain many expensive elements and are difficult to process.

**Table 1**

**Chemical composition of the phases in  $\text{Fe}_{30}\text{Ni}_{20}\text{Mn}_{25}\text{Al}_{25}$  as determined by EDS**

Phase/Element (atomic %)	Fe	Ni	Mn	Al
Matrix (b.c.c.)	$49.1 \pm 1.0$	$1.6 \pm 0.15$	$30.0 \pm 1.0$	$19.3 \pm 1.4$
Plates (B2)	$12.7 \pm 0.5$	$34.3 \pm 0.8$	$13.9 \pm 0.5$	$38.9 \pm 0.9$

**Table 2**  
**Composition and Hardness Measurements of Two Phase Alloy and Constituents**

Alloy Composition	Structure	Vicker's Hardness (VPN)
Fe <sub>30</sub> Ni <sub>20</sub> Mn <sub>25</sub> Al <sub>25</sub>	Two phase B2 and b.c.c.	492±14
Fe <sub>49</sub> Ni <sub>2</sub> Mn <sub>30</sub> Al <sub>19</sub>	b.c.c.	277±33
Fe <sub>13</sub> Ni <sub>34</sub> Mn <sub>14</sub> Al <sub>39</sub>	B2	401±6

The alloy was subjected to mechanical testing at temperatures as shown in Table 3 and  
5 Fig. 3 and the yield strength was obtained.

**Table 3**  
**Yield Strength Sensitivity to Temperature**

Temperature (K)	Yield Strength (MPa)
478	1300
528	1150
553	1400
578	1380
628	1450
628	1470
653	1490
678	1430
728	940
878	300
978	255
1078	200

10

### Example 2

#### Preparation and Characterization of Fe<sub>x</sub>Ni<sub>50-x</sub>Mn<sub>y</sub>Al<sub>50-y</sub> ± 5%

Various alloys have been cast with a composition:

Formula (2)      Fe<sub>x</sub>Ni<sub>50-x</sub>Mn<sub>y</sub>Al<sub>50-y</sub>,

15

wherein X ranges from 15 to 30, and

Y ranges from 20 to 30.



The alloys were cast using the aforementioned arc melting technique. Test results confirm that the miscibility gap forms over a large composition range, and that mechanical and magnetic properties can be manipulated by composition variations in this range. Table 4 lists the alloys evaluated and resulting magnetic and mechanical properties.

**Table 4**

**Hardness, Magnetic Coercivity and Saturation Magnetization of Alloys**

<b>Fe</b>	<b>Ni</b>	<b>Mn</b>	<b>Al</b>	<b>H (VPN)</b>	<b>Coer (G)</b>	<b>Sat. Mag (T)</b>
<b>30</b>	<b>20</b>	<b>20</b>	<b>30</b>	477	8.8	0.11
<b>30</b>	<b>20</b>	<b>30</b>	<b>20</b>	436	56.3	0.12
<b>25</b>	<b>25</b>	<b>20</b>	<b>30</b>	514	0.1	0.2
<b>25</b>	<b>25</b>	<b>30</b>	<b>20</b>	462	99	0.1
<b>25</b>	<b>25</b>	<b>25</b>	<b>25</b>	437	54	0.28
<b>35</b>	<b>15</b>	<b>25</b>	<b>25</b>	467	16	0.29
<b>15</b>	<b>35</b>	<b>25</b>	<b>25</b>	432	54	0.21

In the case of  $\text{Fe}_{30}\text{Ni}_{20}\text{Mn}_{30}\text{Al}_{20}$  Tm with respect to Fig. 1 was empirically determined to be 1544° K

**Example 3**

**Characterization of Spinodal Phase Diagram**

A spinodal phase diagram of the type shown as Fig. 1 may be constructed by varying percentages of Fe, Ni, Mn, Al and M as described in context of Formula (1), except the subscripts a, b, c, d, and e, may be any value. The constituents are processed as described in Examples 1 and 2 to ascertain the presence or absence of spinodal decomposition products, hardness, and magnetic moment. The preferred metals include combinations of Fe, Ni, Mn, and Al, in which case the ranges for X and Y shown in Formula (2) may be any value. When adjusting the respective subscripts a, b, c, d, e, X or Y, it is suggested to increase or decrease the individual ranges or combinations of ranges in steps of five percent from the values shown regarding Formulae (1) and (2), at least until the resulting alloy does not show evidence of spinodal decomposition. It is also possible to repeat the study substituting Co for Ni, in whole or in part, to increase the magnetic moment. For alloys that contain four or five constituents, it is routine in the art that several hundred castings are needed to fully characterize the spinodal phase diagram.

It is understood for purposes of this disclosure, that various changes and modifications may be made to the disclosed embodiments that are well within the scope of the invention. Numerous other changes may be made which will readily suggest themselves to those skilled in the art and which are encompassed in the spirit of the invention disclosed herein and as  
5 defined in the appended claims.

This specification contains numerous citations to references such as patents, patent applications, and publications. Each is hereby incorporated by reference for all purposes.